

Process for producing a catalyst for oxidation of methanol to formaldehyde

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Inventor:
Applicant: PERSTORP AB
Classification:
- international: *B01J23/881; B01J23/882; B01J23/76;*
- european: B01J23/881; B01J23/882
Application number: GB19650041409 19650929
Priority number(s): SE19640015685 19641228

Also published as:

 US3420783 (A1)
 NL6516865 (A)
 FR1454768 (A)
 BE672560 (A)
 NL128440C (C)

more >>

Report a data error here**Abstract of GB1080508**

Iron molybdate catalyst is ground, optionally after air or oven-drying, mixed with water to give a mass containing 37-39% wt. moisture then pelletized with 90 mins. of mixing. The ground molybdate may have a max. particle size of 0.6 mm. Waste molybdate from the pelletizing may be returned to the grinding step. The pellets may have a diameter and axial length of 3.5 mm. The molybdate may be made by mixing solutions of ammonium molybdate and ferric chloride, the ppt. being filtered and washed. The filter cake has a MoO₃/Fe₂O₃ wt. ratio of 5-6, and water content of 55-3 1/2% wt. Drying of this ppt. may be at 80-107 DEG C. The pellets can be dried at 100 DEG C. for 12 hr. to a water content of <5% wt. ALSO: A pelletised iron molybdate catalyst (see Division C1) is used for the oxidation of methanol in excess air to formaldehyde. The formaldehyde produced has a low formic acid content.

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PATENT SPECIFICATION

DRAWINGS ATTACHED

1080,508

1080,508



Date of Application and filing Complete Specification: Sept. 29, 1965.
No. 41409/65.
Application made in Sweden (No. 15685) on Dec. 28, 1964.
Complete Specification Published: Aug. 23, 1967.
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Index at acceptance: —C1 A(D27, G13) AG13D27; C2 C(3A5A, 3A5F3B)
Int. Cl.: —C 01 g 49/00//C 07 c

COMPLETE SPECIFICATION

PATENTS ACT 1949

SPECIFICATION NO. 1,080,508

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated 7 April 1971, this Specification has been amended under Section 14 in the following manner:-

Page 1, delete line 59 insert 'date after oven-drying, the $\text{MoO}_3/\text{Fe}_2\text{O}_3$ weight ratio of the iron molybdate being above 5, mixing'

Page 2, line 112, delete 'optionally'

Page 2, line 113, after 'drying,' insert 'the $\text{MoO}_3/\text{Fe}_2\text{O}_3$ weight ratio of the iron molybdate being above 5,'

Page 3, line 10, after 'catalyst' insert 'in which the $\text{MoO}_3/\text{Fe}_2\text{O}_3$ weight ratio is above 5,'

THE PATENT OFFICE
7 June 1971

R 3376/6

does not have to be...
lyst tubes. One of the disadvantages of said
catalyst is that it is fragile and accordingly
troublesome to transport. The catalyst has
therefore been modified and a precursor cata-
lyst, which is easier to transport, has been
produced. This precursor catalyst contains
more water than the former catalyst and
it requires some activation before it sup-
ports the catalytic oxidation of methanol to
formaldehyde in a satisfactory way. Such
catalysts are described in British Patent
Specification No. 814,073 and United States
Patent Specification No. 2,849,492. No special
steps are required for the activation of the
precursor catalyst as the normal breaking
in period after inserting the precursor into
the catalyst tubes is sufficient to bring about
the necessary activation.
Said catalyst types have been used and
are still in use on an industrial scale. Their
useful life in the tubes is generally about
mass within 90 minutes of mixing the ...
with the ground powder.
To produce the catalyst one may start with
aqueous solutions of, for example, ammonium
molybdate and an iron salt such as iron
chloride. These mixtures are combined to
precipitate iron molybdate, which is then
filtered off and, if necessary, washed. This
is described in the above-mentioned Patent
Specifications and is not included with-
in the scope of the invention.
The filter cake thus obtained and which
suitably has a ratio measured in per cent by
$$\text{weight } \frac{\text{MoO}_3}{\text{Fe}_2\text{O}_3} \text{ of between 5 and 6 may}$$

either be air-dried or dried directly in an
oven. The air-drying, if such step is con-
sidered suitable, is carried out over about

SPECIFICATION AMENDED - SEE ATTACHED SLIP

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PATENT SPECIFICATION

DRAWINGS ATTACHED

1.080.508



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COMPLETE SPECIFICATION

Process for Producing a Catalyst for Oxidation of Methanol to Formaldehyde

We, PERSTORP AB., formerly Skanska Attikfabriken AB, of Perstorp/Sweden, a Swedish Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the production of a catalyst suitable for the oxidation of methanol with an excess of air to formaldehyde. The catalyst comprises iron molybdate.

Such catalysts have been described earlier, for example in United States Patent Specification No. 1,913,405. That Patent Specification is a basic one within the field that it relates to a catalyst consisting, inter alia, of the above-mentioned molybdate. This catalyst is self-supporting and accordingly it does not have to be supported in the catalyst tubes. One of the disadvantages of said catalyst is that it is fragile and accordingly troublesome to transport. The catalyst has therefore been modified and a precursor catalyst, which is easier to transport, has been produced. This precursor catalyst contains more water than the former catalyst and it requires some activation before it supports the catalytic oxidation of methanol to formaldehyde in a satisfactory way. Such catalysts are described in British Patent Specification No. 814,073 and United States Patent Specification No. 2,849,492. No special steps are required for the activation of the precursor catalyst as the normal breaking in period after inserting the precursor into the catalyst tubes is sufficient to bring about the necessary activation.

Said catalyst types have been used and are still in use on an industrial scale. Their useful life in the tubes is generally about

one year. Thereafter they have to be replaced and regenerated or they must be decomposed for the purpose of producing a new catalyst. The useful life of the catalysts is determined by several factors, such as the pressure drop in the catalyst tubes, which increases with time on account of crumbling of the granules. The catalyst granules must not be too small. For this reason the fine catalyst powder is separated before the finished catalyst is used. This powder cannot be used as it is, and it thus constitutes an economic loss.

According to the invention, a process for the production of an iron molybdate catalyst comprises finely grinding iron molybdate, optionally after oven-drying, mixing the ground powder with an amount of water such as to give a moistened mass containing 37—39%, preferably 38%, by weight of moisture, and pelletising the moistened mass within 90 minutes of mixing the water with the ground powder.

To produce the catalyst one may start with aqueous solutions of, for example, ammonium molybdate and an iron salt such as iron chloride. These mixtures are combined to precipitate iron molybdate, which is then filtered off and, if necessary, washed. This is described in the above-mentioned Patent Specifications and is not included within the scope of the invention.

The filter cake thus obtained and which suitably has a ratio measured in per cent by

weight $\frac{\text{MoO}_3}{\text{Fe}_2\text{O}_3}$ of between 5 and 6 may

either be air-dried or dried directly in an oven. The air-drying, if such step is considered suitable, is carried out over about

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two days, and the water content of the filter cake is reduced from approximately 55% to 30% by weight. The humidity or moisture in the filter cake is finally reduced by drying in an oven to below 5%, usually to approximately 3—3 1/2% by weight. The drying is then suitably maintained for two days at a low temperature, about 80°C, and is finished at a temperature of 105—107°C over about one day. If the mass in this stage is set aside for some time, it may again absorb some water and its moisture content may rise to 12% by weight.

The dry filter cake is subjected to a careful fine grinding and sifting, a powder mixture having a maximum particle size of 0.6 mm being obtained. The major part of the mass has, however, a particle size of 0.2—0.3 mm, but it may be highly contaminated with smaller particles. The dry powder mass thus obtained is thereafter mixed with a suitable amount of water before pelletising. This step in the manufacturing process is very critical. The pelletising will fail completely if the mass contains too much or too little water. The limits of the water content are very narrow. The optimum water content is 38% and may deviate therefrom by only plus or minus 1%, that is, the water content must be between 37 and 39% by weight. The water is added as a thin jet, advantageously over a period of not more than ten minutes and preferably within a period of two minutes, while stirring. The way of adding the water is also of importance. At this stage the mass has a temperature of approximately 25°C. If the mass is left in this condition without being further worked, an exothermic reaction starts, and the temperature rises to 50—60°C after a couple of hours. The reaction taking place may suitably be compared with the hardening of cement, and it results in a lumpy product which cannot be pelletised. The mass must therefore be pelletised within at most 90 minutes, preferably within one hour, of mixing the water with the powder. The earlier this can be carried out the better. The pelletising may be performed in any suitable apparatus, for example in a granulating machine such as the Alexanderwerke-granulator. The pellets are preferably cylindrical in form with a diameter and axial length of about 3.5 mm.

The pelletised product may be passed directly into an oven for drying or it may be air-dried during, for example, half a day before the oven-drying. The oven-drying should be carried out at approximately 100°C and should suitably be maintained for a period of twelve hours. The water content of the final product is then lower than 5% by weight.

During granulating and the drying mechanical breakdown of some of the pellets

occurs. The crumbs or particles so formed are returned to the step of fine grinding and are there mixed with the dried filter cake. By this means the manufacturing becomes very economical, as practically no losses occur.

The catalyst obtained by the process according to the invention functions mainly in the same way as former known catalysts of similar type. However, it has advantages over the known iron molybdate catalysts.

As hereinbefore mentioned, the useful life of the known catalysts is limited mainly by the pressure drop which increases with time. The catalyst according to the invention differs appreciably from the known catalysts in this respect. This appears from Figures 1 and 2 of the accompanying drawings. These show the pressure drop measured in metres of water column as a function of the number of days during which the catalyst was on-stream. Curve I relates to the catalyst according to the invention and curve II relates to a known iron molybdate catalyst. Both curves in Figure 1 have been plotted for a space velocity of 12.7 cubic metres gas per litre catalyst per hour, while the space velocity in Figure 2 is 10.9. As is apparent from the Figures, curve I is quite different from curve II. Curve I starts with an appreciably lower pressure drop than curve II and has a much lower slope and finally it runs almost parallel to the abscissa. The advantages of the catalyst according to the invention are accordingly evident in this respect.

A further advantage of the catalyst according to the invention consists in that the end product, the formalin solution, has a lower degree of acidity than that of formalin solutions obtained with known iron molybdate catalysts. This depends on a lower content of formic acid formed.

WHAT WE CLAIM IS:—

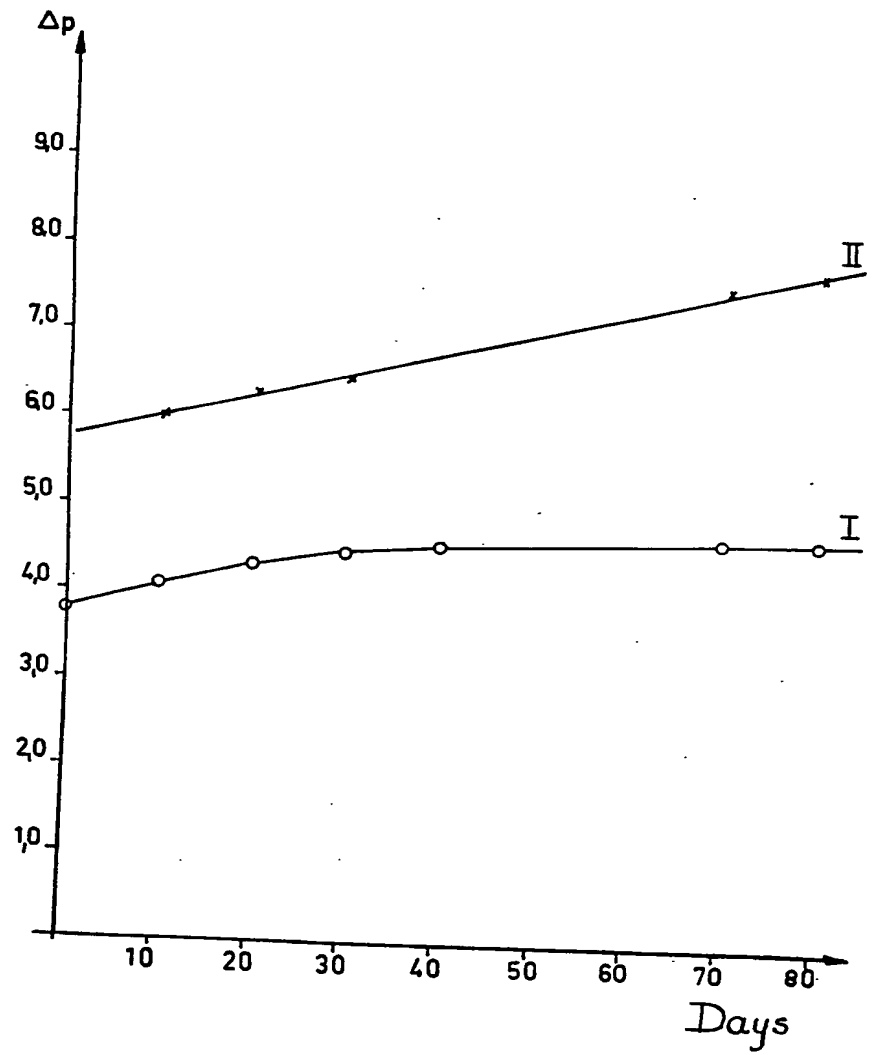
1. A process for the production of an iron molybdate catalyst, which comprises finely grinding iron molybdate optionally after oven-drying, mixing the ground powder with an amount of water such as to give a moistened mass containing 37—39% by weight of moisture, and pelletising the moistened mass within 90 minutes of mixing the water with the ground powder.
2. A process according to claim 1, in which the moistened mass contains 38% by weight of moisture.
3. A process according to either of the preceding claims, in which the pelletising is carried out within 60 minutes of mixing the water with the ground powder.
4. A process according to any one of the preceding claims, in which the mixing of the water with the ground powder is completed within 10 minutes.

5. A process according to any one of the preceding claims, in which the ground powder has a maximum particle size of 0.6 mm.
- 5 6. A process according to any one of the preceding claims, in which the waste after the pelletising is returned to the grinding step.
- 10 7. A process for the production of an iron molybdate catalyst which includes the steps of grinding and pelletising substantially as hereinbefore described.
8. A catalyst whenever obtained by the process claimed in any one of the preceding claims.
9. A process for the oxidation of methanol to formaldehyde in the presence of an iron molybdate catalyst, the catalyst being that claimed in claim 8.
10. Formaldehyde whenever obtained by the process claimed in claim 9.
- 15
- 20

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Agents for the Applicants.

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Fig. 1



1080508 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of
the Original on a reduced scale*
Sheets 1 & 2

Fig. 2

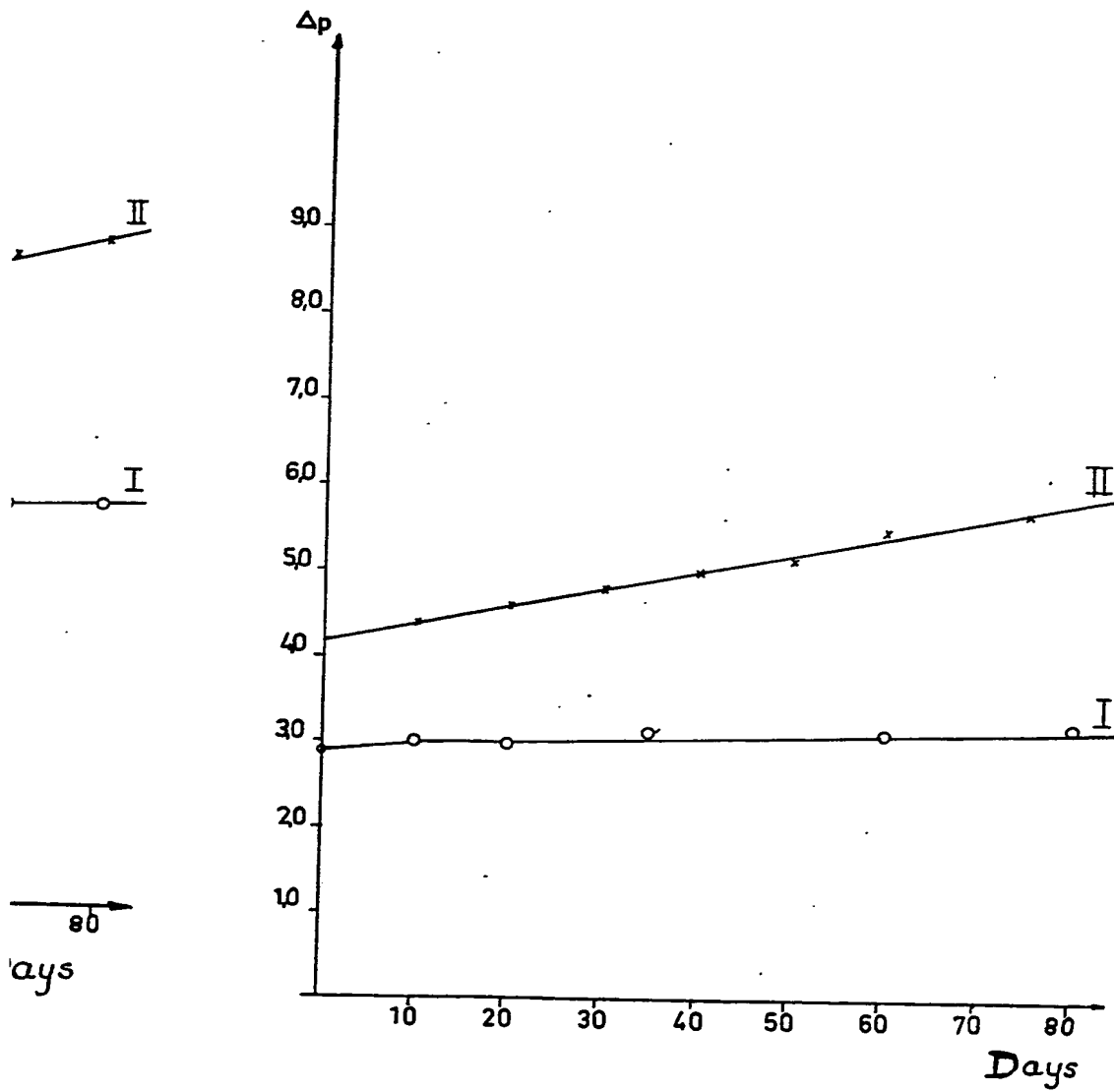


Fig. 1

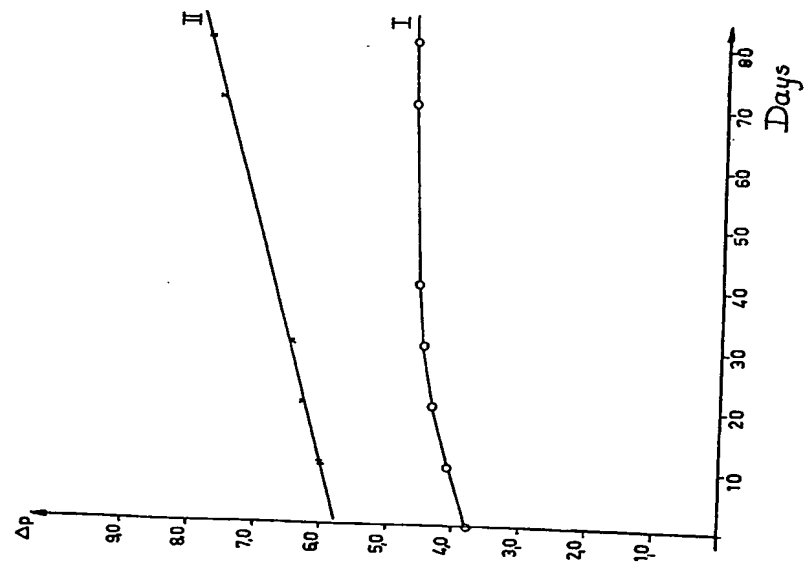


Fig. 2

